

Trace Mineral Ingredients Manufacturing, Quality Concerns, Bioavailability & Formulation

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Introduction

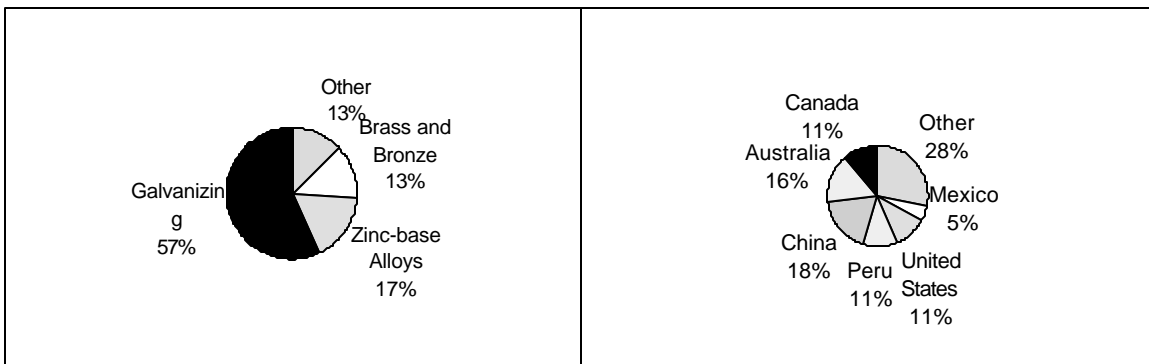
A standard trace mineral premix contains cobalt, copper, iron, manganese, iodine, selenium and zinc. Compounds containing these elements are available from many sources. Knowing your supplier and understanding how the chemical compound was manufactured are key to establishing meaningful specifications and maintaining the quality needed to safely and properly fortify your animal feed.

Zinc Consumption

Zinc is the fourth largest metal consumed in the world (behind iron, aluminum and copper). The United States continues to be the largest consumer of zinc. Zinc is primarily used as a corrosion-protection coating on steel (galvanized metal). In addition, zinc is used in die casting, as an alloying metal with copper to make brass, and in the production of chemicals used in rubber, ceramics, paints, cosmetics, and agriculture. The animal feed industry uses approximately 1% of the total zinc used in the U.S. and approximately 5% of the zinc oxide.

Zinc Production

Forty years ago, the United States was the world's leading miner and smelter of zinc. By 1990, the U.S. represented only 7% of world mine output and 5% of world smelter capacity. Mine production in Alaska has increased. Typically, the U.S. relies heavily on Canada, Mexico, and Peru, since it imports 50% of its zinc requirement. The U.S. is the world's largest importer of refined zinc.



(A) Domestic Uses of Zinc (2000)

(B) Zinc Production (2000)

Production of Animal Feed Grade Zinc Products

The forms of zinc most commonly used in animal feed are zinc oxide and zinc sulfate.

Zinc oxide suitable for animal feed use is usually manufactured by the Waelz Kiln Process. Here, zinc-bearing ores are roasted, forming a zinc fume. The zinc fume is collected in a large collector and is densified through an additional process. The very high temperatures used in this process drive off most of the residual heavy metals. A very pure zinc oxide can be manufactured by the French Process. French Process zinc oxide is made by oxidizing pure zinc metal to zinc oxide.

The French Process usually results in material that is higher in zinc (e.g. 78-80% zinc). It is a light powder, which makes it very hard to handle in animal feed mixes. French Process zinc oxide is generally more expensive on a per-unit-of-zinc basis.

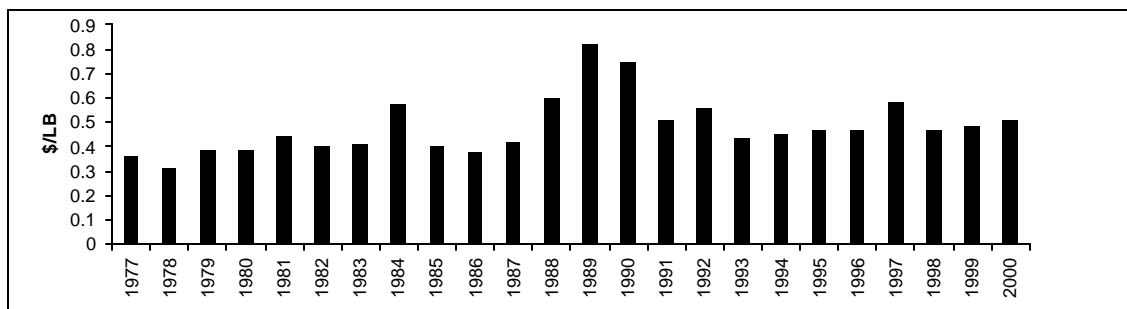
Zinc sulfate is usually manufactured from secondary zinc sources. In this case, zinc is dissolved in sulfuric acid, precipitated and spray dried.

Factors Affecting Zinc Pricing and Supply

The price of zinc metal generally follows the economy since most zinc is used in automotive and construction-related applications. Average annual zinc metal prices have varied from \$.35-\$.80/lb during the past 20 years. Since most feed grade zinc sulfate is made from secondary sources, changes in zinc metal pricing have a less immediate effect on zinc sulfate than on zinc oxide. Zinc sulfate pricing and supply, however, can be influenced by fertilizer demand during the fertilizer season. Increasing emphasis on reducing zinc oxy sulfate use in fertilizers is increasing the demand for zinc sulfate and, thereby, tightening the supply. This has put some upward pressure on zinc sulfate prices.

Feed grade zinc oxide supplies are ordinarily plentiful. Zinc sulfate can get tight in April and May during the peak fertilizer season. Ample lead times should be allowed during this period.

Average Zinc Prices



Function of Zinc in the Animal Feed Industry

Zinc is a functional component of several enzyme systems, including those involved with respiration, cellular growth, reproduction and digestion.

Typical Deficiency Symptoms of Zinc in Animals

Foot rot	Reduced immune response
Reduced conception rate	Severe dermatitis
Reduced growth rate	Parakeratosis (thickening of skin epithelial cells)

Typical Toxicity Symptoms of Zinc in Animals

Diarrhea	Pneumonia
Arthritis	Reduced hemoglobin formation
Reduced growth rate	

Typical Mineral Interactions with Zinc

Excessive calcium reduces zinc metabolism. Copper and iron are slightly antagonistic to zinc. Dietary plant phytate/phytic acid reduces zinc availability.

Major Sources of Zinc Approved by AAFCO for Use in Animal Feed

SOURCE	ZINC CONTENT	COLOR
Zinc Oxide	72%	Various
Zinc Sulfate	35.5%	White

Zinc Oxide Specification Guidelines

	Zinc	Arsenic	Lead	Mercury	Cadmium	Antimony
AFIA	72%	250 ppm	500 ppm	1 ppm	80 ppm	-
AAFCO	-	10-800 ppm	100-2000 ppm	1 ppm	80-500 ppm	10 ppm
ANAC	72%	250 ppm	500 ppm	1 ppm	200 ppm	10 ppm

Zinc Sulfate Specification Guidelines

	Zinc	Arsenic	Lead	Mercury	Cadmium	Antimony
AFIA	35.5%	10 ppm	50 ppm	1 ppm	100 ppm	-
AAFCO	-	10-800 ppm	100-2000 ppm	1 ppm	80-500 ppm	10 ppm
ANAC	-	10 ppm	50 ppm	1 ppm	50 ppm	1 ppm

Quality Considerations

Toxic elements including cadmium, lead, mercury, and arsenic should be monitored and be below industry standards. Cadmium levels in zinc sulfate should not exceed 100 ppm and typically should run below 50 ppm. Lead levels in zinc oxide should be below 500 ppm.

Zinc metal is not an AAFCO-approved source of zinc. Zinc metal content in zinc oxide should not exceed 1%. Many zinc by-product materials (including zinc metal) that are used as raw material for zinc sulfate can find their way into the animal feed industry in an unprocessed state. They should not be accepted as equivalent alternatives to feed grade zinc oxide or zinc sulfate.

Recently Chinese zinc sulfate has been imported into the U.S. The quality of this material varies from good to unacceptable. In China there are many small factories that produce zinc sulfate. Some factories do a great job separating the lead and cadmium from the zinc. Others do a poor job. In the U.S. we have seen cadmium levels in Chinese zinc sulfate as high as 20,000-30,000 ppm.

Color is not a good indicator of zinc oxide quality. Quality sources can be white, tan, brown, green, reddish, or black.

Other Comments

Zinc oxide is the most widely-used source of zinc in the animal feed industry. It has the highest zinc content and is the most economical source on a per-unit-of-zinc basis. Zinc is frequently the highest total cost trace mineral in animal feed.

Zinc metal is pyrophoric and may oxidize rapidly, causing combustible material to burn. Zinc oxide, on the other hand, does not burn. Zinc sulfate is water soluble.

DOT-Hazardous Materials (Class 9) include zinc sulfate which, when shipped in packages of 1,000 pounds or more, is reportable.

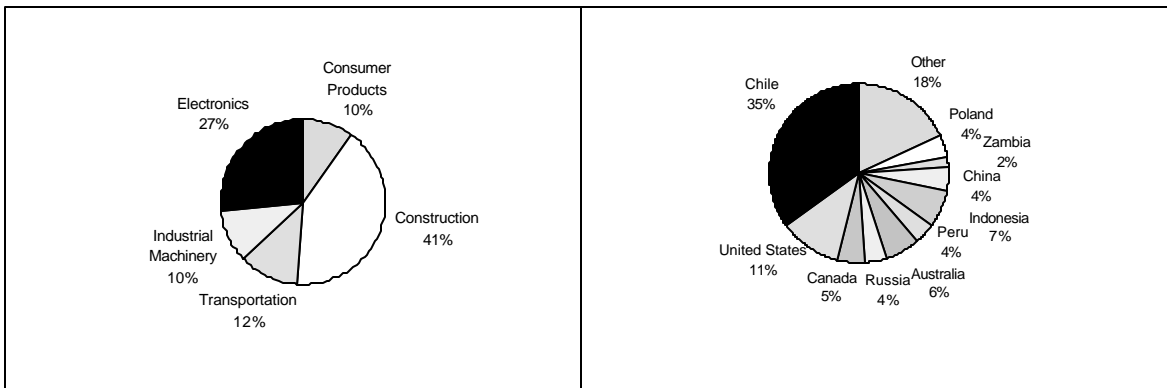
Copper Consumption

Copper metal ranks third in world metal consumption (behind iron and aluminum). The primary use of copper is in electrical cables and wires. Over 70% of U.S. copper consumption is for such use whether it be within electronic, construction, or other industries. Approximately 43% of the United States' copper consumption comes from secondary copper. The animal feed industry represents substantially less than 1% of total U.S. copper consumption.

Copper Production

Copper smelting operations have been traced back to 5000 BC. Primary copper metal is mined from copper bearing ores often containing only 0.5-3% elemental copper. These ores are smelted (melted or fused to extract the metal), producing primary copper metal containing 100% elemental copper. Major copper mining countries include the U.S. and Chile. At least 10 mines in Chile have increased their capacities in 1997 and 1998.

Domestic mine production in 2000 declined to 1.45 million metric tons, a 25% deduction from 1996. Approximately 99% of all domestic production of copper is recovered from mines located in four states: Arizona, Utah, New Mexico and Montana. The U.S. imports approximately 10% average of its copper metal requirements. Western Europe, the U.S., and Japan are the major copper consumers.



(A) Domestic Uses of Copper Metal (2000)

(B) Copper Production (2000)

Production of Animal Feed Grade Copper Products

The forms of copper most commonly used in animal feed are copper sulfate, copper oxide, copper carbonate, and tribasic copper chloride.

Copper sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) can be manufactured from copper metal, copper scrap or as a co-product from the LIX system, which reclaims secondary copper from spent etchant solutions. Most feed grade copper sulfate is made from the LIX process.

There are two common forms of copper oxide, cupric oxide (CuO) and cuprous oxide (Cu₂O). Copper oxide is manufactured by roasting copper metal in an oxidizing furnace or by solubilizing copper metal with acid and treating it with a caustic to precipitate copper oxide.

Copper carbonate (CuCO₃) results from adding sodium carbonate to copper sulfate solutions.

Tribasic copper chloride (Cu₂(OH)₃Cl) is a relatively neutral salt of copper that is produced from a solution of copper by crystallization. Feed stock can come from copper containing hydrochloric acid solutions (acidic based) or from copper containing ammonium chloride solutions (alkali based).

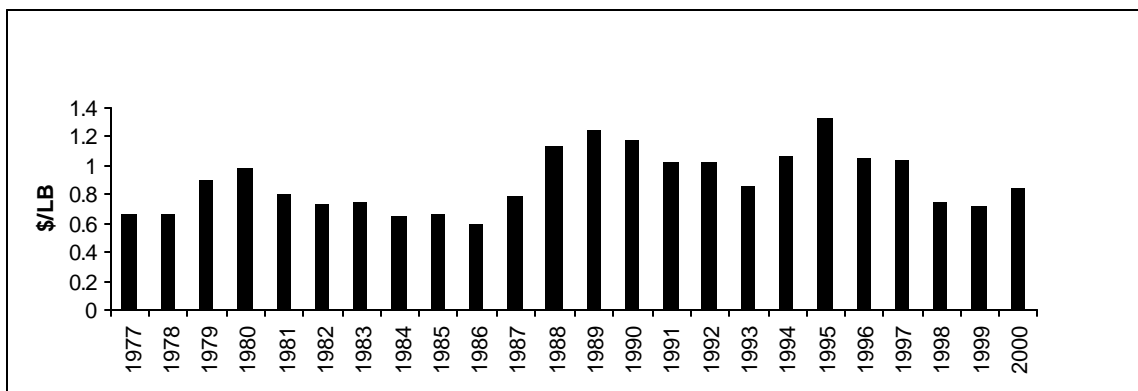
Factors Affecting Copper Pricing and Supply

The worldwide economy is often a good indicator of the strength of the copper metal market, especially the housing, transportation and construction sectors. Localized mining strikes, plant shut downs or start-ups, environmental problems, political and social unrest, and government bids can all affect the pricing of copper. During the last 20 years, copper metal prices ranged from \$.35-\$1.65/lb, with average annual prices in the \$.60-\$1.30/lb range. Copper is considered to be a semi-precious metal and its price can vary widely when the precious metals market is in turmoil. Copper metal is traded on exchanges like gold and silver. This can lead to rapid fluctuations in copper pricing.

Copper metal pricing usually increases as spring construction season starts. Pricing of the individual feed derivatives normally follows copper metal pricing. However, each derivative is more significantly impacted by its available production capacities, product demand, and other factors within its own sub-market.

Supply of the individual forms of feed grade copper derivatives can vary greatly. Copper carbonate supply is frequently tight, whereas copper oxide supply is typically plentiful.

Average copper metal pricing (based on Comex)



Function Of Copper in the Animal Feed Industry

Copper is a nutritional requirement for the production of hemoglobin and for the normal growth and well being of the animal. Copper is a component of enzyme systems, including those involved with cardiac functions. Supplemental rates higher than nutritional levels are frequently recommended for use in poultry and swine for growth performance or therapeutic benefits.

Typical Deficiency Symptoms of Copper in Animals

Reduced iron mobilization/anemia	Reduced growth rate
Spontaneous fractures/bowed legs	Reduced fertility/reproductive dysfunction
Poor hair coat/lack of pigmentation	

Typical Toxicity Symptoms of Copper in Animals

Weight loss	Depression, weakness, lethargy
Dehydration	Danger of over concentrating copper in sheep
Jaundice	Morbidity in sheep

Typical Mineral Interactions with Copper

Molybdenum reduces copper uptake and increases copper excretion and forms insoluble copper/molybdenum complex. Low dietary zinc and iron and high calcium accentuate copper toxicity; iron and zinc compete with copper for binding sites during absorption.

Major Sources of Copper Approved by AAFCO for Use in Animal Feed

SOURCE	COPPER CONTENT	COLOR
Copper Sulfate	25.2%	Blue
Copper Oxide	75%	Black
Copper Carbonate	55.4%	Green
Tribasic Copper Chloride	58%	Green

Copper Sulfate Specification Guidelines

	Copper	Arsenic	Lead	Mercury	Cadmium	Nickel	Antimony
AFIA	25.2%	7 ppm	9 ppm	-	2 ppm	100 ppm	-
AAFCO	-	3-100 ppm	9-600 ppm	1 ppm	2-100 ppm	100 ppm	0-20 ppm
ANAC	25%	10 ppm	60 ppm	1 ppm	20 ppm	100 ppm	20 ppm

Copper Oxide Specification Guidelines

	Copper	Arsenic	Lead	Mercury	Cadmium	Nickel	Antimony
AFIA	75%	70 ppm	3000 ppm	-	60 ppm	-	50 ppm
AAFCO	-	3-100 ppm	9-600 ppm	1 ppm	2-100 ppm	100 ppm	0-20 ppm
ANAC	75%	100 ppm	300 ppm	6 ppm	60 ppm	100 ppm	20 ppm

Copper Carbonate Specification Guidelines

	Copper	Arsenic	Lead	Mercury	Cadmium	Nickel	Antimony
AFIA	Not Established for AFIA.						
AAFCO	-	3-100 ppm	9-600 ppm	1 ppm	2-100 ppm	100 ppm	0-20 ppm
ANAC	55%	5 ppm	150 ppm	1 ppm	5 ppm	100 ppm	20 ppm

Tribasic Copper Chloride Specification Guidelines

	Copper	Arsenic	Lead	Mercury	Cadmium	Nickel	Antimony
AFIA	Not Established for AFIA.						
AAFCO	-	3-100 ppm	9-600 ppm	1 ppm	2-100 ppm	100 ppm	0-20 ppm
ANAC	-	50 ppm	10 ppm	1 ppm	1 ppm	10 ppm	20 ppm

Quality Considerations

High quality sources have proper particle size, a low dust factor, and high flowability. Arsenic and cadmium levels are frequently high in some imported sources of copper sulfate. Lead, mercury and other toxic element levels should be monitored in copper oxide. High free acid levels in copper sulfate may cause it or premixes it is used in to set up. Free acid also causes paper packaging to deteriorate. Copper metal is not approved by AAFCO for use in animal feed.

Tribasic copper chloride should not be used in the same system that makes sheep mixes, unless extremely good clean out measures are assured. Products with extremely fine particle size should be tested in equipment to insure proper flow and dispersion and that the product does not “get lost” in the system.

Other Comments

Copper sulfate and tribasic copper chloride are the most bioavailable forms of copper. Both are generally preferred for monogastric applications. Copper oxide is the most economical form on a per-unit-of-copper basis, but is not as bioavailable as the other forms. Copper sulfate accounts for the most significant trace mineral cost in broiler feed.

Copper carbonate production is not as steady and plentiful as other copper products. Therefore, product availability can become a problem at times. Production capacity of tribasic copper chloride is expandable, but limited. Tightness in supply can occur.

The AFIA has not established guidelines for copper carbonate and tribasic copper chloride. AAFCO would use the same guidelines as copper oxide and copper sulfate.

DOT-Hazardous Materials (Class 9) include copper sulfate which, when shipped in packages containing 1,000 lbs. or more, is reportable.

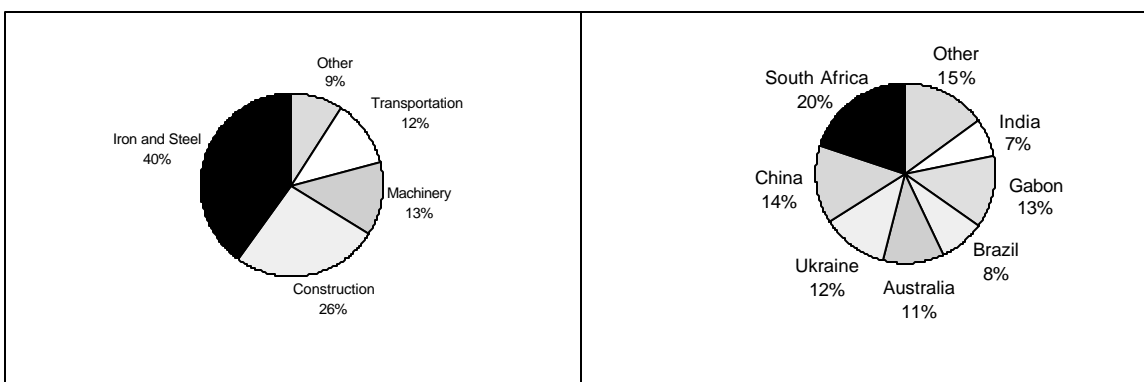
Manganese Consumption

Manganese is essential to iron and steel production. Iron making and steel making account for 90% of U.S. manganese demand. Among a variety of other uses, manganese is a key component of some widely-used aluminum alloys and is used in the oxide form in dry cell batteries. The animal feed industry accounts for approximately 1% of U.S. manganese consumption.

The majority of the countries which are large consumers of manganese do not have a local source available and import all their needs either in the form of ore, which is processed in the country, or as alloys, which have already been refined and are designated for the steel industry.

Manganese Production

South Africa, China, Australia, and the Ukraine are the largest manganese-producing countries in the world. However, some of these countries produce a low grade ore. Major U.S. import sources of manganese include higher grade products from Gabon, Australia, South Africa, and Mexico. The U.S. imports almost all of its manganese ore.



(A) Domestic Uses of Manganese (2000)

(B) Manganese Production (2000)

Production of Animal Feed Grade Manganese Products

The forms of manganese most commonly used in animal feed are manganous oxide and manganese sulfate monohydrate. Manganous oxide (MnO) is manufactured by roasting the natural manganese dioxide (pyrolusite) in a reducing atmosphere. Toxic elements in the natural, high-grade ore are low and generally of no concern.

Manganese sulfate ($MnSO_4$) can be manufactured by dissolving natural manganese carbonate or reduced manganous oxide in acid or as a co-product of certain

chemical operations. Some manganese sulfate streams originate as a co-product of anisic aldehyde production.

Factors Affecting Manganese Pricing and Supply

The price of manganese ore follows the demand generated by the strength of worldwide economies, especially steel demand. Historically, it has been relatively steady. The manganese market is sensitive to the development of techniques in the steel industry. Manganese sulfate is less sensitive to manganese ore prices than is manganous oxide.

U.S. manganous oxide capacity and demand have been in close sync in the mid-90's. Product has been available, but there has been very little excess capacity. Manganese sulfate supply is normally ample except for tight supplies during the spring fertilizer season. Lead times on manganese sulfate orders should be extended in April and May.

Function of Manganese in the Animal Feed Industry

Manganese is a functional component of many enzyme systems, including those involved with carbohydrate, protein and lipid metabolism. In addition, manganese is a component of the matrix of bone and essential for reproductive function. Manganese is necessary for utilization of biotin, vitamin B₁ and vitamin C.

Typical Deficiency Symptoms of Manganese in Animals

Abnormal skeletal growth/paralysis	Reduced milk production
Poor reproductive performance	Poor egg shell formation
Small, weak offspring	Slipped tendons in poultry
Increased fat deposition	

Typical Toxicity Symptoms of Manganese in Animals

Growth depression	Abortion
Depressed feed intake	Abdominal discomfort

Typical Mineral Interactions with Manganese

High manganese increases iodine excretion and reduces iron absorption. Excess calcium and phosphorus inhibit manganese absorption. Iron and cobalt slightly reduce manganese availability.

Major Sources of Manganese Approved by AAFCO for use in Animal Feed

SOURCES	MANGANESE CONTENT	COLOR
Manganous Oxide	60%	Green-Brown
Manganese Sulfate	32%	Cream-Tan

Monohydrate		
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Manganous Oxide Specification Guidelines

	Manganese	Arsenic	Lead	Cadmium	Antimony
AFIA	60%	70 ppm	50 ppm	-	-
AAFCO	-	2-100 ppm	1-90 ppm	1-20 ppm	70-200 ppm
ANAC	60%	70 ppm	100 ppm	20 ppm	200 ppm

Manganese Sulfate Monohydrate Specification Guidelines

	Manganese	Arsenic	Lead	Cadmium	Antimony
AFIA	27-31.5%	0.5 ppm	20 ppm	-	-
AAFCO	-	2-100 ppm	1-90 ppm	1-20 ppm	70-200 ppm
ANAC	30%	30 ppm	20 ppm	10 ppm	100 ppm

Quality Considerations

Some imported sources of manganese sulfate have been known to be lumpy and, in some cases, dusty. Manganese dioxide content in manganous oxide should be below 2%. Manganous oxide from lower grade ores (e.g. 55% manganese content) should be monitored for heavy metals.

Other Comments

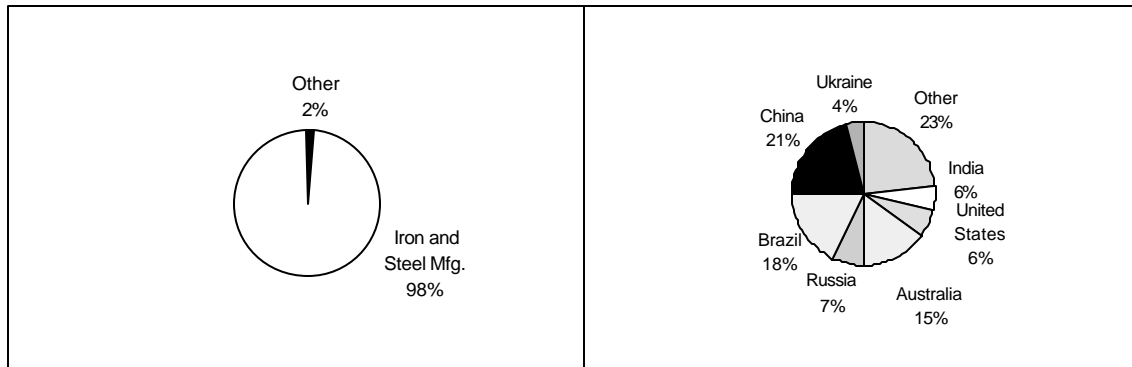
Manganous oxide is used in more animal diets than any other source of manganese. Manganous oxide has high manganese content, low toxic elements, good biological availability and, on a per-unit-of-manganese basis, is the least expensive source of manganese available. When water solubility is necessary, manganese sulfate is preferred. Manganese dioxide is not considered biologically available to the animal. Manganese carbonate is not used in animal feed because of its low bioavailability. Manganese chloride is extremely hygroscopic and is not used because it is very difficult to handle.

Iron Consumption

Nearly all iron ore consumed in the world is used in the manufacturing of iron and steel. The balance is used in the manufacturing of cement, heavy-medium materials, pigments, ballast, agricultural products, or specialty chemicals.

Iron Ore Production

U.S. iron ore production is driven by demand from the steel industry. Major world producers of iron ore include China, Brazil, and Australia. Iron is the fourth most abundant rock-forming element and composes about 5% of the Earth's crust. Evidence suggests that iron is more abundant in the inner part of the Earth and has combined with nickel to make up the majority of the planet's core.



(A) Domestic Uses of Iron (2000)

(B) Iron Ore Production (2000)

Production of Animal Feed Grade Iron Products

The forms of iron most commonly used in animal feed are ferrous sulfate monohydrate and ferrous carbonate.

The blast furnace has remained the principal instrument used in converting iron ore to molten iron since colonial times. The principal forms of iron for feed grade products are siderite, ilmenite, and hematite. Ferrous carbonate (siderite) is mined from domestic ore. The ore is mined as ferrous carbonate (FeCO_3); however, atmospheric conditions can convert the ferrous carbonate (FeCO_3) to hematite (Fe_2O_3). Mined ferrous carbonate is air dried, crushed, ground, and packaged.

Ferrous carbonate is mined from an open pit mine and late winter rainy conditions can disrupt the mining, drying, and grinding operations and, therefore, product availability.

Ilmenite is a titanium bearing iron oxide. Major world sources are in Norway and Sweden. Ilmenite ore is dissolved in acid and the titanium is extracted. The remaining solution of liquid ferrous sulfate is crystallized as a multiple hydrate of ferrous sulfate ($\text{FeSO}_4 \cdot \text{XH}_2\text{O}$). This material is shipped to the U.S. where it is dried to monohydrate and heptahydrate forms. During the last 20 years, the feed industry has switched from using heptahydrate to monohydrate ferrous sulfate.

Hematite is an iron oxide that is used to color feed. Iron oxide can also be produced synthetically yielding various intensities of red, yellow and black. Natural iron oxide is produced from ore that is mined, crushed, dried, ground, and packaged. Synthetic iron oxide is manufactured by roasting ferrous sulfate crystals. Iron oxide in animal feed should be used as a colorant and not as a source of iron.

Factors Affecting Iron Pricing and Supply

The price of iron ore follows the demand generated by the steel industry, but this has little impact on feed grade products.

Ferrous sulfate pricing is dependent upon titanium dioxide production, currency exchange rates and ocean freight, as well as normal manufacturing cost increases. Product is readily available since one of the two major U.S. ferrous sulfate manufacturers brought a new plant on line in 1996. Ferrous sulfate is also used in the fertilizer industry.

The only domestic source of iron carbonate is mined in eastern Texas. The open pit mining operation is subject to considerable flooding during the rainy season (January-March). This can affect product supply and moisture content in late winter and early spring. Efforts to upgrade mining equipment, drying capabilities, and storage capacity are ongoing in order to minimize supply disruptions.

Function of Iron in the Animal Feed Industry

Iron functions in the transport of oxygen through the blood and in the respiratory processes through its oxidation-reduction activity and its ability to transport electrons.

Typical Deficiency Symptoms of Iron in Animals

Anemia	Rough hair coat
Reduced immune response	Muscle weakness
Reduced weight gain	

Typical Toxicity Symptoms of Iron in Animals

Reduced water intake	Sweating
Reduced feed intake	Lethargy
Nervous system disorder	Abdominal swelling

Typical Mineral Interactions with Iron

High iron induces cobalt, copper, manganese, selenium, and zinc deficiency. High dietary cadmium, copper, iodine, manganese, phosphorus, and zinc reduce iron availability. Nickel deficiency reduces iron uptake in young pigs.

Major Sources of Iron Approved by AAFCO for Use in Animal Feed

SOURCE	IRON CONTENT	COLOR
Ferrous Sulfate Heptahydrate	20%	Greenish
Ferrous Sulfate Monohydrate	30%	Light Gray
Ferrous Carbonate	38%	Tan-Brown

Ferrous Sulfate Heptahydrate Specification Guidelines

	Iron	Fe ₂ O ₃	Arsenic	Lead	Mercury	Free Acid
AFIA	21%	0.4-0.8%	0.5 ppm	5 ppm	-	0.13-0.19%
AAFCO	-	-	1-50 ppm	1-90 ppm	1 ppm	-

Ferrous Sulfate Monohydrate Specification Guidelines

	Iron	Fe ₂ O ₃	Arsenic	Lead	Mercury	Free Acid
AFIA	31%	1-2%	1 ppm	7 ppm	-	0.2-0.4%
AAFCO	-	-	1-50 ppm	1-90 ppm	1 ppm	-
ANAC	30%	-	5 ppm	10 ppm	1 ppm	-

Ferrous Carbonate Specification Guidelines

	Iron	Fe ⁺³	Arsenic	Lead	Mercury	Cadmium	Antimony
AFIA	40%	3%	0.5 ppm	1 ppm	-	41 ppm	0.5 ppm
AAFCO	-	-	1-50 ppm	1-90 ppm	1 ppm	-	-
ANAC	38%	-	40 ppm	70 ppm	1 ppm	50 ppm	25 ppm

Quality Considerations

Some ferrous sulfate sources are high in free acid that can cause the material to set up. It can also cause the paper bag that the product is packaged in to disintegrate. Some sources of ferrous sulfate are dusty and can create environmental and employee health problems. Ferrous sulfate heptahydrate is hygroscopic and will set up. Use it only when necessary. Both ferrous sulfate heptahydrate and monohydrate are water soluble, but the heptahydrate has a faster rate of solubility than the monohydrate.

Iron carbonate is a less expensive form of iron on a per-unit-of-iron basis, but iron sulfate is a more bioavailable source of iron. Iron oxide is a colorant only. It is not a bioavailable source of iron. As iron carbonate oxidizes, it turns reddish in color and loses some of its bioavailability.

Other Comments

DOT-Hazardous Materials (Class 9) regulations include ferrous sulfate when shipped in packages of 1,000 lbs. or more.

Ferrous sulfate and choline chloride combined in the same concentrated mix can cause the mix to set up.

References

Prince Agri Products, July 2001, Trace Mineral Overview
Complete text available upon request (prince@princeagri.com).